

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Graft Copolymers and method of making them

We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention pertains to synthetic, fiber-forming high polymers, particularly to graft or block-type copolymers exhibiting improved dyeability and reduced static charge.

Hydrophobic polymeric materials of varying origin are commonly employed in the manufacture of various synthetic shaped articles including, films, ribbons, fibres filaments, yarns and threads which hereinafter will be illustrated with particular reference to fibres. Non-aromatic hydrocarbon, polyolefin polymers may be utilized with great advantage for such purposes.

The polyolefin materials that are contemplated as being adapted for utilization as substrates in the practice of the present invention include any of the non-aromatic hydrocarbon olefin polymers, such as polyethylene and polypropylene that have been prepared from monomeric, non-aromatic hydrocarbon monoolefin monomers containing from 2 to 8 carbon atoms in their molecule. It is especially advantageous to utilize a polypropylene composition, particularly a fiber-forming variety, such as an unbranched stereospecific polymer for this purpose.

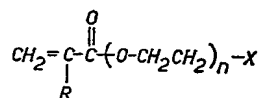
Difficulty is often encountered in dyeing or coloring synthetic hydrophobic fibers that have been prepared from non-aromatic, hydrocarbon olefin polymers. This is especially so when it is attempted to obtain relatively deeper shades of coloration in the finally dyed product.

Various techniques have been evolved for providing polyolefin compositions of improved dyeability. The practice of such techniques has not always been completely satisfactory.

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Neither have the products achieved thereby always provided a completely suitable solution to the problems involved. For example, many of the fiber products which are prepared in accordance with the above-identified techniques known to the art often have inferior physical properties when they are compared with those prepared from unmodified polyolefin polymers. Also, such products, once they have been prepared, may not be as receptive as might be desired to a wide range of dyestuffs, due to inherent limitations in the materials capable of being employed for enhancing dye-receptivity.

In accordance with the present invention, there is provided a textile fiber of improved dyeability comprised of a 2 to 8 carbon monoolefin polymer containing appendant graft polymer segments of one or more monomers of the formula



wherein R is hydrogen or methyl, X is halogen, hydroxyl, alkoxy, acrylate, methacrylate or a 1 to 4 carbon alkyl radical and n has an average value between 18 and 200. In the more preferred compositions of the invention the monoolefin polymer is a polymer of propylene.

The dye receptive graft copolymers of the invention are conveniently prepared by graft polymerizing monomer in intimate contact with the polymeric substrate. It is desirable to bring the substrate in the form of a fine fiber into intimate contact with the monomer, preferably in aqueous dispersion for graft polymerization. It may be advantageous to expose the substrate to ozone or high energy ionizing radiation prior to the contacting treatment with the monomer.

As is apparent, the graft copolymer substituent that is combined with the polyolefin substrate lends the desired receptivity of and sub-

stantivity for various dyestuffs to the compositions while the non-aromatic, hydrocarbon, polyolefin trunk substrate that is so modified facilitates and secures the excellent physical proportions and characteristics of the various shaped articles, including fibers into which the compositions may be fabricated. Advantageously, as mentioned, the polyolefin substrate that is modified by graft copolymerization is polypropylene.

As a general rule, it is desirable for the graft copolymer to be comprised of at least 80 per cent by weight of the polyolefin substrate. In many instances, it may be satisfactory for the graft copolymer composition to be comprised of between 85 and 95 per cent by weight of the polyolefin substrate, particularly, when it is polypropylene. In this connection, however, better dyeability may generally be achieved when the grafted copolymeric substituents are prepared under such conditions that they have relatively long chain lengths. Thus, it is usually preferable, when identical quantities of grafted substituents are involved, for relatively fewer, but longer chain length grafts to be available than to have a greater number of substituents of relatively shorter chain length.

As mentioned, the fibers of the invention have remarkably good dye-receptivity, particularly in view of their polyolefin origin. In most cases, for example, the dye-receptivity of the fibers of the present invention is improved to such an extent in comparison with unmodified polyolefins, particularly unmodified polypropylene, that a color differential of at least about 30 Judd units, may readily be obtained. The Judd unit, a measure of extent of coloration, is described and defined by D. B. Judd in an article in the "Americal Journal of Psychology", Vol. 53, page 418 (1939). More applicable data appears in "Summary on Available Information on Small Color Difference Formulas" by Dorothy Nickerson in the American Dyestuff Reporter, Vol. 33, page 252 (June 5, 1944). See also "Interrelation of Color Specifications" by Nickerson in the "Paper Trade Journal," Vol. 125, page 153 for November 6, 1947.

Besides having excellent physical properties and other desirable characteristics, the fibers of the present invention similarly have the indicated high capacity for being readily and satisfactorily dyed to deep and level shades of coloration with many dyestuffs. For example, fibers of the present invention may be easily and successfully dyed according to conventional procedures using acid, vat, acetate, and naphthol dyes. Such dyestuffs, by way of illustration as Colour Index 61710 (formerly Colour Index 1080), Colour Index Vat Violet 2, Colour Index 35527, Colour Index Azoic Diazo 11 and Colour Index Sulfur Brown 12 may advantageously be employed.

Other dyestuffs, that may be utilized beneficially on fiber products of the invention in-

clude basic dyes such as Colour Index Basic Green 1 and Colour Index Vat Blue 35; vat dyestuffs such as Colour Index Vat Blue 5, Colour Index Vat Violet 2, Colour Index Vat Green 1, a soluble vat dyestuff; acetate dyes as Colour Index Dispersed Orange 5, Colour Index Dispersed Red 13, Colour Index Dispersed Red 15, Colour Index Dispersed Blue 1, and Colour Index Dispersed Yellow 32.

The dyed textile fiber products, are generally lightfast and are well imbued with good resistance to crocking.

The dye-receptive graft copolymers may be prepared and provided by swelling or impregnating the polyolefin substrate with the monomeric substance then polymerizing the monomer in situ in the substrate. Advantageously, this may be accomplished when the substrate is in the form of an already shaped fiber or filamentary structure. Beneficially, the graft copolymerization of the impregnated monomer may be accomplished and facilitated with the assistance of a polymerization catalyst or catalyzing influence, which preferentially interacts with the substrate in order to establish or form grafting sites thereon and simultaneously or subsequently initiate the graft copolymerization. As a practical matter, it is generally most desirable to form the graft copolymer compositions in such manner. Most of the free radical generating chemical catalysts, including peroxide and persulfate catalysts, and actinic radiations, including ultraviolet light, may be utilized for the desired graft copolymerization. It may often be exceptionally advantageous, however, to accomplish the graft copolymerization by subjecting the monomer-impregnated polyolefin substrate to a field of high energy radiation in order to efficiently provide an effectively attached graft copolymer of the polymerized monomeric impregnant on the hydrophobic polyolefin substrate. Excellent results may also be achieved by activating the polyolefinic polymer substrate prior to contact with the monomer so as to generate or create free radical sites upon the substrate to which the monomer may attach in order to from the graft polymerized substituents. Such activation, as is known, may be accomplished by means of preirradiation in fields of high energy radiation (including ultra-violet light) or by exposing the polyolefin substrate to the influence of oxygen (in the presence of ultraviolet light) or to already formed ozone prior to contact with the graft copolymer-forming monomer.

The monomer may be intimately impregnated in the polyolefin substrate in any desired manner prior to the graft copolymerization. Thus, the monomer may be directly applied, particularly when it has a swelling effect on the substrate, or it may be applied from dispersion or solution in suitable liquid vehicles, preferably those tending to swell the polymer, until a desired monomer content has been ob-

5 tained. Ordinarily, it is advantageous for the monomer to be diluted in a solvent or dispersant vehicle so as to provide a treating bath in which to swell or impregnate the polyolefin substrate with the latter being immersed in the bath for a sufficient period of time to attain a desired monomer content adequate for the intended purpose. The polyolefin substrates, as has been mentioned, may be in any fabricated or unfabricated form. Unfabricated graft copolymer compositions may be converted to the fibers of the invention by any desired technique adapted for such purpose with conventional polymers. It is generally desirable and of significant advantage, however, to impregnate a preformed textile fiber of the polyolefin (or a cloth or fabric comprised thereof) with the monomer in order to prepare the graft copolymer fibers of the invention.

10 In this connection, particularly when preformed fiber structures are involved, the article may be in any desired state of formation for the impregnating and graft copolymerizing modification. Thus the fibres may be treated before or after any stretch has been imparted thereto. In addition, they may be in various stages of orientation, or in a gel, swollen or dried condition.

15 The impregnation and succeeding polymerization may, in general, be effected at temperatures between 0°C. and about 200°C. for periods of time ranging up to 4 or more hours. The most suitable conditions in each instance may vary according to the nature and quantity of the specific monomeric impregnant involved and the graft copolymerizing technique that is utilized. For example, when chemical catalysts are employed for purposes of forming the graft copolymer, a temperature of between about 50° and 100°C. for a period of time between about 15 and 45 minutes may frequently be advantageously employed for the purpose. Under the influence of high energy radiation, however, it may frequently be of greatest advantage to accomplish the graft copolymerization at temperatures between about 20 and 60°C. utilizing relatively low dose rates and total dosages of the high energy for the desired purpose. Graft copolymerization on preactivated substrates may ordinarily be accomplished by simply exposing the activated substrate to the monomer (preferably in concentrated solution) at an elevated temperature until the graft copolymerized substituents have formed on the substrate.

20 When the graft copolymer compositions are prepared from preformed or already shaped polyolefin polymer substrates that are successively impregnated with the monomer, which is then graft copolymerized in situ in the shaped article, excess monomer, if desired, may be squeezed out or removed in any suitable manner prior to effecting the graft copolymerization.

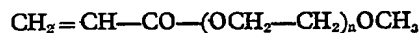
25 The chemical free radical generating cata-

lysts which may be employed with greatest advantage in the preparation of the graft copolymer compositions include hydrogen peroxide, benzoyl peroxide, cumene hydroperoxide, ammonium or potassium persulfate. Such catalysts may be used in conventional quantities to effect the graft copolymerization. When they are utilized, it is of greatest benefit to incorporate them in the impregnating solution of the monomer that is used.

30 The high energy radiation which may be employed for inducing the graft copolymerization for the preparation of the graft copolymers is of the type which provides emitted particles or photons having an intrinsic energy of a magnitude which is greater than the planetary electron binding energies that occur in the graft copolymerizing materials. Such high energy radiation is available from various radioactive substances which provide beta or gamma radiation as, for example, radioactive elements including cobalt-60 and cesium-137 or nuclear reaction fission products. If it is preferred, however, high energy radiation from such sources as electron beam generators, including linear accelerators and resonant transformers, or X-ray generators may also be utilized. It is beneficial to employ the high energy radiation in a field of at least about 40,000 roentgens per hour intensity. A roentgen, as is commonly understood, is the amount of high energy radiation as may be provided in a radiation field which produces in one cubic centimeter of air at 0°C. and 760 millimeters of absolute mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation (when the secondary electrons are fully utilized and the wall effect of the chamber is avoided). It is most desirable, incidentally, to graft copolymerize all or substantially all of the monomeric impregnant to and with the polymer substrate being modified in order to provide the compositions of the present invention. In addition, as has been indicated, particularly when preactivation of the substrate is performed, ultraviolet light may also be employed as the high energy radiation form including its use in combination with oxygen or ozone.

EXAMPLE 1

35 A fine fiber sample of 4 denier melt spun polypropylene was ozonated by being exposed for one hour at room temperature to a stream of oxygen that contained from 2 to 6 per cent ozone. The ozone in the oxygen stream was generated by passing oxygen through a 7,500 volt electric arc. The polypropylene in the fiber had an apparent molecular weight of about 200,000 (as determined by viscosity) and a crystalline melting point of about 110°C. After having been ozonated so as to cause activation of the polymer by generation of free radical sites on its surface, the fiber sample was immersed in a 40 per cent aqueous suspension of a monomer of the structure:



wherein n had an average value of about 18 being derived from a polyethylene glycol ether of 600 molecular weight. The fiber was maintained in the monomeric dispersion for a period of about 4 hours at a temperature of 100°C. It was then removed from the monomer suspension, rinsed thoroughly with water, dried and subsequently dyed in the conventional manner with 4 per cent Colour Index Disperse Red 1. Excellent results were achieved with the graft copolymerized fiber product having deep and level shades of coloration. In contrast, the unmodified polypropylene yarn was only slightly stained with the same dyestuff. The graft copolymerized fiber product was also dyed well to deep and level shades of coloration with Colour Index 353, a direct dye and a basic dye Colour Index Basic Red 14. The improvement in dye-receptivity between the graft copolymerized fiber products of the present invention in comparison with unmodified polypropylene was such that a colour differential of about 25 Judd units was obtained between the Colour Index Disperse Red 1 dyed graft copolymer composition and the unmodified polypropylene fiber.

EXAMPLE 2

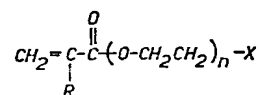
The procedure of Example 1 is duplicated excepting to accomplish the graft copolymerization under the influence of an electron beam from a Van de Graaff generator operated at 2 million electron volts to effect a total dosage of about 10 Mrep at a dose of about 5 Mrep per minute. Identical results are obtained.

Results similar to the foregoing may also

be obtained when any other of the mentioned varieties of the monomeric polyglycol esters of acrylic and methacrylic acids are utilized in a similar manner in place of those set forth in the above examples and when graft copolymers are prepared with such monomers on unfabricated forms of the polymer substrate or when the monomers are utilized with other varieties of non-aromatic, hydrocarbon olefin polymers.

WHAT WE CLAIM IS:—

1. Textile fiber of improved dyeability comprising of a 2 to 8 carbon monoolefin polymer containing appendant graft polymer segments of one or more monomers of the formula



wherein R is hydrogen or methyl, X is halogen, hydroxyl, alkoxy, acrylate, methacrylate or a 1 to 4 carbon alkyl radical and n has an average value between 18 and 200.

2. Textile fiber as claimed in Claim 1 wherein n has an average value of 18.

3. Textile fiber as claimed in either of claims 1 or 2 wherein the monoolefin polymer is a propylene polymer.

4. Textile fiber of improved dyeability as claimed in Claim 1 substantially as described with reference to the specific Examples.

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